Vapor Pressure of Tektite Glass and Its Bearing on Tektite

Trajectories Determined From Aerodynamic Analysis

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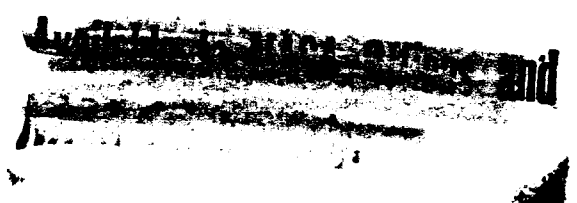
Abstract

Various experiments have been conducted to resolve a large discrepancy between two measurements that have been reported for the vapor pressure of tektite glass. This discrepancy affects significantly the trajectories and mode of tektite origin determined from aerodynamic ablation calculations. It is shown that measurements in a furnace of vaporization rate relative to that of four different standards (SiO_2, TiO_2, Au, Ag) yield mutually concordant results for tektite vapor pressure. Also, measurements in an arc jet of the stagnation temperature, the rate of surface recession, and the mass loss during aerodynamic ablation are in mutual agreement with the results from vaporization rate measurements. Further, observations of flash boiling under certain experimental conditions, and of no boiling in others, provide a bracketing of tektite vapor pressure that likewise is compatible with the other measurements. Over the temperature range of the present experiments, $1700°$ to $3000°K$, a least-squares fit to the data is represented by $P_v(atm) = exp[18.5 - 57,400/T(°K)]$. These various experimental results demonstrate that the measurements by Walter and Carron [1964] of the pressure for incipient bubbling do not represent tektite vapor pressure, but some bubble pressure instead that at some temperatures is as much as a million times higher than the vapor pressure. The recent aerodynamic calculations by Adams and Huffaker [1964] of very shallow, grazing tektite trajectories, which are based on Walter's bubble-pressure measurements, are therefore erroneous.

Earlier calculations by Chapman and Larson [1963] of relatively steep, direct-entry trajectories are not affected significantly by the new vapor pressure data.

INTRODUCTION

The conclusion from aerodynamic analysis that the atmosphere entry trajectories of Australian tektites correspond to origin directly from the moon [Chapman, 1960; Chapman and Larson, 1963] depends, in part, on having correct knowledge of the vapor pressure of tektite glass. In reaching this conclusion, Chapman and Larson used the amount of ablation observed on australites together with several other measurable quantities of aerodynamic significance to determine the initial velocity and initial angle of entry into the earth's atmosphere. Since these initial quantities prescribe the tektite's trajectory in space, and the trajectory fixes the place of origin, the reliability of the conclusion of lunar tektite origin depends upon having employed adequately accurate values for all physical properties that affect aerodynamic ablation, including specific heat, viscosity, and thermal conductivity, as well as vapor pressure. Chapman and Larson reported measurements of all these properties and checked them by aerodynamic ablation experiments. The vapor-pressure measurements were made by Centolanzi, using a relative rate of vaporization technique, with fused silica as the standard.

Recently, however, Walter [1964] measured the pressure for incipient bubbling in tektite glass, and represented these data as

vapor pressure. His measured bubble pressures $P_V(b)$ are very different indeed from the measurements of the vapor pressure $P_V(\dot{m})$ made previously by Centolanzi. A comparison of the two vapor pressure determinations, as illustrated in Figure 1, shows that the discrepancy between the measurements is extraordinary - amounting, in fact, to a factor of approximately one million at 1700°K. Such a large difference, of course, would imply that if Walter's measurements of bubble pressure represent tektite vapor pressure, then the aerodynamic trajectories determined by Chapman and Larson are inaccurate, and their conclusion of lunar tektite origin uncertain. In some recent aerodynamic calculations, Adams and Huffaker [1964] employed as vapor pressure some measurements of bubble pressure by Walter - without testing them against any measurements of tektite ablation - and obtained greatly different trajectories, namely, extremely shallow ones of a type that graze the edge and skip through the earth's atmosphere. In contrast, relatively steep trajectories of the direct-entry type were obtained by Chapman and Larson. The large difference between the two sets of measurements of vapor pressure, therefore, affects conclusions as to the mode of tektite origin.

Inasmuch as vapor pressure measurements at high temperature on any compound comprising such a complex mixture as tektite glass are not free of complications, some possible objections can be envisioned against almost any technique. Walter's measurement of bubble pressure within tektite glass, for example, need not necessarily represent the vapor pressure, inasmuch as it is well known that bubbling can arise

from a variety of circumstances other than boiling, such as from

dissolved or adsorbed gases, or from the presence of minor

impurities much more volatile than tektite glass. Likewise,

Centolanzi's determination of vapor pressure from measurements of

the rate of vaporization, relative to the silica standard he

employed, can be in error if the vapor pressure of the standard

happens to be wrong; also it must be certain that such an experi-

ment is conducted in the diffusion controlled regime, rather than

the free-molecule regime, in order to avoid uncertainties contrib-

uted by the coefficient of vaporization which is not known presently

for tektite glass.

The objective of the present research is to resolve the dis-

crepancy between the two values reported for tektite vapor pressure

by conducting three independent types of experiment. First, tektite

vapor pressure is determined by the rate-of-vaporization technique

in which TiO_2, Au, and Ag standards are employed in addition to

the SiO_2 standard previously used; moreover, these measurements are

conducted under experimental conditions demonstrated to be in the

diffusion controlled regime. Second, results of aerodynamic experi-

ments with tektite glass in an arc jet are presented in which

measurements of surface temperature, of recession rate, and of mass

loss are compared with corresponding results calculated for various

vapor pressures. Such a comparison evaluates directly whether or

not a given vapor pressure yields correct results in ablation cal-

culations, and hence in trajectory determinations. In an appendix

to an earlier publication Chapman [1964] made a similar comparison using Walter's bubble pressure for tektite vapor pressure which yielded results grossly incompatible with ablation experiments. This comparison is extended herein to conditions of higher velocity and temperature that constitute a test more than adequately severe for the conditions of tektite entry flight. Third, some experiments are described in which, at certain temperatures and pressures of melted tektite glass, boiling is not observed, while at other temperatures and pressures vigorous flash boiling is observed. Such observations bracket the vapor pressure within a certain range and provide thereby a third test independent of the two other types of experimental evidence. In a final section of this paper the bearing of tektite vapor pressure on the trajectories deduced from aerodynamic analysis is discussed.

<div align="center">APPARATUS</div>

Measurements of the vaporization rate for tektite glass relative to various standards were made in a resistance heated furnace. As illustrated in Figure 2, a cylindrical heater element made of tantalum provided a test zone 1.3 cm diameter by 5.1 cm long. The test cavity temperature was measured with an optical pyrometer through a hole in the heater element arranged to act as a blackbody, and could be controlled up to a maximum of about $2500^{\circ}K$. The furnace atmosphere was argon of variable pressure between the limits of 10^{-4} and 1 atm.

Fig. 2

Crucibles for the test samples were constructed of rhenium, a metal remarkably resistant at high temperatures to chemical combination with either tektite glass or any of the reference standards used. Several crucibles were used repeatedly, and when the glass was dissolved out of the crucible after each run by immersion in hydrofluoric acid no change in weight of the crucibles could be measured on a balance of 5 μg sensitivity. Typical measurements of mass vaporized ranged in hundreds of micrograms. The crucibles, therefore, remained chemically inert in these experiments.

Aerodynamic ablation experiments were performed in three different arc-heated supersonic jets providing overall a wide range in test conditions of pressure and heating rate. One of the facilities has been described in detail by Shepard and Winovich [1961] and was employed in previous ablation experiments [Chapman and Larson, 1963]. Of the other two arc jets, one was used to provide relatively low pressures at which tektites boil, and the other to provide relatively high heating rates at which the vapor pressure has a major effect on the measured rate of ablation.

EXPERIMENTAL PROCEDURE AND RESULTS

Various experiments performed in the high-temperature furnace and in the arc-heated wind tunnels combine to provide three independent methods of determining the vapor pressure of tektite glass: from measurements of vaporization rate relative to standards, from measurement of aerodynamic ablation characteristics, and from

observations of bracketing conditions which are either above or below the boiling point of tektite glass. Methods of reducing the data and the results obtained are discussed separately in the three sections which follow.

Determination of vapor pressure from relative rates of vaporization. Vaporization at a fixed temperature in a furnace increases with an increase in vapor pressure of the substance, but decreases with an increase in the ambient pressure of the furnace. The dependence upon ambient pressure is illustrated in sketch (a). At very low pressures a substance of molecular weight M vaporizes in the free molecule regime at a rate approaching some maximum $\dot{m}_{vac}$ as the ambient pressure approaches zero. This vacuum rate does not necessarily equal the rate $P_V\sqrt{M/2\pi RT}$ given by the original kinetic theory equation of Langmuir, unless the evaporation coefficient $\alpha_{vap} = \dot{m}_{vac}\sqrt{2\pi RT}/P_V\sqrt{M}$ is unity. Thus measurements of mass-loss rate in the free molecule regime require knowledge of α_{vap} in order to yield information on vapor pressure. At higher ambient pressures, however, the rate of mass loss no longer is limited by evaporation rate, but by a diffusion process, and as a result decreases with increasing ambient pressure. The principal ablation of a tektite during its atmosphere entry flight occurs in the diffusion-controlled regime. In this regime, the mass-loss rate - and hence the vapor pressure determined therefrom - is not affected by the evaporation coefficient.

<sketch (a)

The basic theory behind measurements of vapor pressure from vaporization rate relative to that of standards of known vapor pressure is quite simple. In the diffusion-controlled regime the mass-loss rate for fixed aerothermal conditions, that is, for fixed convection currents and fixed temperature, is proportional to the product of diffusion coefficient D, molecular weight M, and vapor pressure P_V. (See, e.g., Eckert [1959] for a discussion of the principles involved.) Inasmuch as the diffusion coefficient in kinetic theory [Chapman and Cowling, 1939] is proportional to the quantity $\sqrt{(M + M_A)/MM_A}$ where M_A is a molecular weight of the ambient atmosphere into which the substance is diffusing, it follows that the ratio of mass-loss rate of a substance to that of some standard (subscript s) is simply

$$\frac{\dot{m}}{\dot{m}_s} = \frac{DMP_V}{(DMP_V)_s} = \sqrt{\frac{M}{M_s}\left(\frac{M + M_A}{M_s + M_A}\right)} \frac{P_V}{P_{V_s}}$$

The principal approximation in this equation is that the sum of the effective molecular sizes of the diffusing and ambient-medium molecules are substantially the same as for the standard. As Chapman and Cowling show, even for extremely wide variations in molecular weight (from 2 to 130), and wide differences in molecule structure (from monatomic to complex polyatomic molecules), this particular sum varies only by a factor equivalent to a variation in P_V of about ±2. For a standard of reasonably similar molecular structure to that of the substance to which it is compared, the corresponding factor of uncertainty in P_V would be much less. Even an uncertainty

factor of ± 2 in P_V is trivial compared to the large difference being investigated between the two discrepant values reported for tektite vapor pressure.

In order to illustrate the wide applicability, and the degree of accuracy, of the particular technique employed, measurements have been made on a number of liquids whose vapor pressure is well known. For these tests a crucible containing each liquid was placed in a chamber at room temperature and 1 atm pressure. Some typical raw data on the measured mass loss as a function of time are shown in Figure 3. The slopes of these curves yield the mass-loss rate $\dot{m}$ which is related linearly to the vapor pressure P_V according to the equation previously developed. The Knudsen number, expressed as the ratio of mean free path to characteristic dimension of the diffusion chamber, is so small in these experiments that such conditions certainly are in the diffusion controlled regime. A plot of the handbook value of vapor pressure versus our measurements of $\dot{m}$ is shown in Figure 4. The proportionality of P_V and $\dot{m}$ clearly extends over the full range of about five orders of magnitude covered by these data. Moreover, the scatter in the data points for various liquids amounts to a factor of roughly ± 2, as pointed out earlier. It follows, for example, that if any one of these liquids were chosen as the 'standard,' then the vapor pressure of any of the other liquids could be determined to within a factor of ± 2 simply from the corresponding ratio of mass-loss rates. Actually, the factor involving the square roots of molecular weights is rather
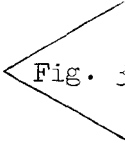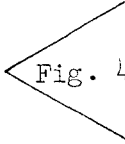
Fig. 3

Fig. 4

insensitive, and, if omitted, would not change the result appreciably. These data, as well as the data for tektite glass described later, have been plotted separately both with and without this molecular-weight factor, and very little difference was found. With the particular technique employed, the use of more than one standard obviously should improve the probable accuracy of the results.

Having established the basic method, we now apply it to determine the vapor pressure of tektite glass. It is readily demonstrated in which regime - diffusion controlled, free molecule, or transitional - such determinations are made, simply by varying the ambient pressure. Most of the data presented subsequently were taken at a furnace pressure of 1/2 atm. Proof that at this pressure the vaporization of tektite glass is indeed diffusion controlled is shown in Figure 5. Throughout the pressure range of these measurements, both well below and above 1/2 atm, the mass loss clearly decreases with increasing pressure in the manner (constant negative slope on log-log plot) characteristic of the diffusion-controlled regime, rather than either the free molecule (zero slope) or transitional regime (variable slope). Diffusion control should be expected, in fact, inasmuch as the Knudsen number for these furnace experiments is very small compared to unity, approximately 2×10^{-5} at 1/2 atm.

Fig. 5

Some typical raw data illustrating the relative rates of vaporization are presented in Figure 6. These data are for a temperature of $1700^{\circ}K$, and a pressure of 10^{-4} atm. The observed nonlinearity of the curves near zero time is due to the time required for the sample

Fig. 6

(a function principally of sample size) to attain essentially constant temperature because of its finite mass. It is clear, for example, that the steady-state mass-loss rate for silver (0.19 g/cm²-min) is higher than that for gold (0.036 g/cm²-min); and this is as expected since the vapor pressure of silver is correspondingly higher than that of gold at this temperature. In sharp contrast, the mass-loss rate for tektite glass and for silica are much lower $(1.3 \times 10^{-5}$ g/cm²-min) than that for either gold or silver. If the vapor pressure of tektite glass were as high as Walter's bubble pressure measurements, the mass-loss rate for tektite glass should be 12 g/cm²-min, more than ten times that of silver. In contrast, the actual values are about 10,000 times less, regardless of whether gold, silver, or silica is employed as a standard; and hence Walter's bubble pressure must be several hundred-thousand times higher than the tektite vapor pressure at this temperature.

Entirely consistent results have been obtained at other pressures and temperatures. The data are illustrated in Figure 7. It is to be observed that the determination of vapor pressure for 10^{-4} atm and 1/2 atm at 1700°K both give essentially the same results, indicating that the level of furnace pressure does not affect the determination of vapor pressure, from which it follows that either tektite vaporization is diffusion controlled down to pressures the order of 10^{-4} atm, or else α_{vap} is approximately the same for tektite glass and all the standards employed. Of considerable significance is the fact that the results obtained, using four different
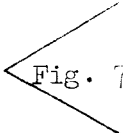
Fig. 7

standards - gold, silver, titania (rutile), and silica - are all

consistent in indicating that the tektite vapor pressure does not

differ greatly from that of silica.[1] The fact that Walter's bubble-

pressure data are many orders of magnitude higher than all of these

P_V data for tektite glass means that the bubbles in Walter's melted

tektite glass certainly contained not only tektite vapor but also

some other vapors of much more volatile matter, hence, that Walter's

bubble-pressure data do not represent vapor-pressure data of tektite

glass.

Determination of vapor pressure from measurements of tektite

ablation in an arc jet. When tektite glass ablates during exposure to

severe rates of aerodynamic heating, several different quantities

can be measured which provide an independent determination of vapor

pressure. Such a determination, however, requires that all other

physical properties affecting aerodynamic ablation be known, such

as density, viscosity, thermal conductivity, and specific heat.

Each of these quantities for tektite glass has been measured pre-

viously [Chapman and Larson, 1963], and each measurement was inde-

pendently checked by a different ablation experiment: the specific

heat by rate of temperature rise prior to the onset of ablation,

the thermal conductivity by the steady-state temperature during

ablation, the viscosity by the rate of ablation under test

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[1]The equation employed for vapor pressure of silica is that

listed by Hidalgo [1960], namely, $l_nP_V(atm) = 18.5 - 57,800/T(^{\circ}K)$,

which corresponds to a slightly lower vapor pressure than the

equation listed by Schick [1958].

conditions where vaporization was negligible, and the vapor pressure by the weight loss during an ablation experiment under other test conditions where vaporization was appreciable. It is emphasized that the arc-jet ablation experiments provide not only an independent test of the vapor pressure of tektite glass, but also a direct test of the accuracy of aerodynamic calculations for determining the entry trajectories and hence the place of tektite origin.

The difference between the bubble-pressure function and the vapor pressure as measured by the rate of vaporization technique is so great that even the most insensitive of the measurable quantities during aerodynamic ablation proves unambiguously that the bubble pressure function is an erroneous representation of tektite vapor pressure. The surface temperature at the stagnation point is probably the least sensitive quantity, and, for this reason, can be calculated most easily and with considerable accuracy. When a model is suddenly exposed to an arc-jet stream, the surface temperature T_s increases rapidly with time and attains a steady-state value within about 6 to 8 sec. The quantity actually measured is the energy E_r radiated from the stagnation point, which is expressed for convenience in terms of the equivalent black-body temperature, or 'brightness' temperature, T_b, defined as $T_b^4 = \sigma E_r$, where σ is the Stefan-Boltzmann constant. The surface temperature T_s is related to the brightness temperature and the emissivity ϵ through the equation $\epsilon T_s^4 = T_b^4$. In a typical ablation experiment T_s exceeds T_b by about $200°$ to $300°C$. The experimental measurements

of temperature are compared with calculations employing the same ablation program (described recently by Matting and Chapman [1965]) and high-speed digital computer as that used in previous computations [Chapman and Larson, 1963; Chapman, 1964]. In Figure 8 the measurements of surface brightness temperature are compared with calculations for various vapor pressure functions, including different multiples of the function $P_V(\dot{m})$ determined from vaporization rate data, as well as the function $P_V(b)$ determined from Walter's bubble-pressure data. Measurements were made on both synthetic and natural tektite glass at stagnation-point test conditions of: enthalpy, 1,370 cal/g; pressure, 0.35 atm; heating rate, 86 cal/cm^{2}sec; and radius of curvature, 0.95 cm. It is evident from Figure 8 that the computed temperatures are in reasonable agreement with experiment, for vapor pressures within a factor of about 10 from $P_V(\dot{m})$ but the temperatures computed for the bubble-pressure function are about 440° too low. This is an independent demonstration that $P_V(b)$ is higher than the true vapor pressure of tektite glass, by at least several orders of magnitude, since there is no possibility for an error as large as 440° in the experiments or calculations. Thus the measurements of temperature during aerodynamic ablation in an arc jet confirm the experimental results from rate of vaporization relative to standards, namely, that Walter's bubble pressure is far higher than the vapor pressure of tektite glass.

A more sensitive test from aerodynamic ablation experiments of the correct vapor pressure is provided by measurements of the amount

Fig. 8

of vaporization, that is, the mass loss during an ablation experiment.
This quantity readily is measured by weighing a model both before
and after an experiment. Such measurements provide an excellent
check on the vapor pressure, since the rate of vaporization, and
hence mass loss, varies sensitively with the vapor pressure. The
results of mass-loss measurements on 13 different experiments,
including both natural and synthetic tektite models, are presented
in Figure 9. Test conditions at the stagnation point for these
experiments were: enthalpy, 2330 cal/g; pressure, 0.37 atm; heat-
ing rate, 175 cal/cm^{2}sec; and radius of curvature, 0.95 cm. In
the calculations of mass loss, as represented by the dashed lines
in this figure, allowance was made for the variation in vaporization
rate over the front face of the model, since this rate is greatest at
the stagnation point and diminishes at the outer areas of the front
face. The ratio of stagnation-point vaporization $\dot{m}_s$ to the average
vaporization rate $\dot{m}$ was determined experimentally for geometrically
similar models of fused silica and this same ratio applied to the
models constructed of tektite glass. Such a procedure yields
results good to approximately a factor of 2 in mass loss. Such an
uncertainty is trivial compared to the great differences between
$P_V(b)$ and $P_V(\dot{m})$. The data in Figure 9 show that the measured mass
loss (which varied from about 1 to 3 mg, depending upon the test
time) agrees with that computed for the function $P_V(\dot{m})$ to within
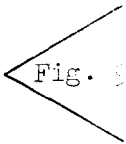a factor of about 2 or 3. In contrast, the computed mass

Fig. 9

loss for the bubble-pressure function $P_V(b)$, shown near the

ordinate of this figure, is greatly in error; the function $P_V(b)$

yields vaporization rates which are too high by a factor of over

100. For example, the computed mass loss for $P_V(b)$ at a test

time of 8 sec is 120 mg, whereas the measurements fall in the

range of approximately 1 mg. These experiments show that the

correct vapor pressure to use in tektite ablation calculations

cannot be significantly greater than $P_V(\dot{m})$ and may, in fact, be

as much as a factor of 2 or 3 less - in a range not far from the

vapor pressure of silica. These measurements of mass loss, there-

fore, constitute one further experimental demonstration that

Walter's bubble pressure $P_V(b)$ is orders of magnitude higher than

the true vapor pressure of tektite glass.

The most important test insofar as aerodynamic and trajectory

calculations are concerned is provided by measurements of the rate

of aerodynamic ablation. Such measurements have been conducted in

two different arc jets. In one the stagnation-point enthalpy was

2700 cal/g; the pressure, 0.24 atm; the heating rate, 156 cal/cm^{2}sec;

and the radius of curvature, 0.95 cm. The corresponding data are

presented in Figure 10 for both synthetic and natural tektite glass.

As in the previous figure, the dashed lines represent the computed

amount of ablation for various P_V, ranging from 1/10 of $P_V(\dot{m})$

to 100 times $P_V(\dot{m})$, and also including the computations for the

bubble-pressure function $P_V(b)$. It is seen that the calculated

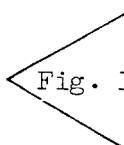amount of ablation for $P_V(\dot{m})$ agrees reasonably well with the

Fig. 10

measurements, that is, to within the order of ±10 per cent, the
approximate degree of repeatability of the measurements; but the
calculations for a vapor pressure ten times that of $P_V(\dot{m})$ or
greater are in poor agreement with the experiments. In particular,
the amount of ablation calculated for the bubble-pressure function
$P_V(b)$ is only one-third of the experimental values, thereby con-
stituting a direct proof that the use of Walter's bubble pressure
in aerodynamic calculations will yield highly inaccurate determina-
tions of the atmosphere entry trajectories of tektites. Inasmuch
as the recent calculations of Adams and Huffaker [1964] were made
with a vapor-pressure function based on the bubble-pressure measure-
ments of Walter, it follows that their determination of tektite
trajectories are erroneous. The magnitude and direction of the error
involved is discussed later.

Some additional ablation experiments conducted both on tektite
glass and fused silica at higher enthalpies provide a further test
of the appropriate vapor pressure of tektite glass, and extend the
experimental confirmation of $P_V(\dot{m})$ to considerably higher temperatures.
The measurements of ablation presented in Figure 11 correspond to
stagnation-point test conditions of: enthalpy, 11,000 cal/g; pressure,
0.52 atm; heating rate, 760 cal/cm^{2}sec. It is noted that this
particular enthalpy is equivalent to a flight velocity of 9.6 km/sec,
closely representing that at which peak heating occurs during a
tektite entry flight from the moon. Calculations using the same
computing program have been made for both silica and tektite glass,
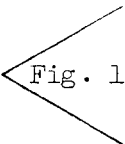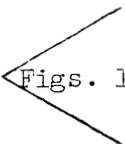
Fig. 11

employing the physical properties of silica as listed by Hidalgo [1960]. The calculations for silica agree reasonably well with the corresponding measurements, and show the ablation rate to be much less than that for tektite glass under the same test conditions, principally because of the much higher viscosity of silica. In this figure the corresponding measurements for tektite glass are compared with computations for different P_V functions, corresponding, in this case, to a range in the ratio $P_V/P_V(SiO_2)$ from 0 to 10. These calculated curves bend upward somewhat because, as the ablation proceeded, the radius of curvature varied from 1.6 cm initially to 0.9 cm after 10 sec of ablation; whereas the corresponding curves for silica are essentially straight, since the radius of curvature for the silica model remained essentially constant (1.6 cm). The value of vapor pressure most closely agreeing with the data corresponds to a vapor pressure approximately one-half that of silica, which would be about one-fourth $P_V(\dot{m})$ for tektite glass. This particular determination represents the lowest single value for the vapor pressure of tektite glass relative to that of silica determined in the course of this investigation. It is regarded as no more reliable, however, than the other determinations, inasmuch as the calorimeter used in this particular test, unlike that in all other tests, happened to be of sufficiently different size that nonuniformities in the flow stream could render the heating rate about twice as uncertain (± 20 per cent, estimated) as the heating rates in the other data. Nevertheless, the value

determined for P_V is lower than $P_V(\dot{m})$ whereas the bubble pressure P_V is much higher; thus we have one more experimental result confirming the essential validity of the rate of vaporization measurements as opposed to the bubble-pressure measurements. Since the computed ablation temperature for these experiments is $3040^{\circ}K$, higher than for a tektite entry flight, the range of experimental confirmation of vapor pressure is thereby extended to temperatures encompassing those encountered during atmosphere entry.

Observations of boiling in arc-jet experiments. From the preceding it is clear that $P_V(b)$ is very much higher than the true vapor pressure of tektite glass. This implies that some bubbling, other than true boiling, was observed in Walter's experiments. Bubbling, in fact, is to be expected inasmuch as tektites are known to contain dissolved volatiles (H_2O, H_2, CO_2, and CO have been observed to evolve from tektites heated in a vacuum). It is of interest, then, to investigate true boiling of tektite glass under laboratory conditions and to determine whether such observations are consistent with the vapor pressure determined from other data.

Under proper test conditions, tektite glass boils in an arc-jet ablation experiment, provided sufficiently low pressures are reached. Such experiments provide a 'yes-no' test, that is, an indication of either boiling, or no boiling, and thereby a means of bracketing the vapor pressure curve, between certain limits. A salient feature of using ablation to melt tektite glass is that it automatically exposes the fresh, uncontaminated interior of the

glass. There is no possibility of contamination by adsorbed or absorbed gases, or other impurities, such as frequently exists when tektite glass samples are ground or otherwise prepared in the laboratory. The process of vaporization at the stagnation point precludes boiling there, but not elsewhere on a model. In approximately 100 experiments over the past few years we have never observed signs of boiling at the stagnation point of ablated models of natural tektite glass. Hence, measurements of stagnation temperature and pressure during ablation correspond to conditions of no boiling. The two models shown in Figures 12(a) and (b) correspond to such conditions; they are completely free of any indication, even under the microscope, of boiling or other vesiculation. Therefore, since the measured pressure for (b) is 0.05 atm, and the measured brightness temperature 2150°K, corresponding to a surface temperatue 2310°K, we can say that at a temperature of 2310°K, the boiling pressure, and hence vapor pressure, is certainly less than 0.05 atm. Such data provide an upper bound to vapor pressure. On the vapor pressure versus reciprocal temperature plot these points are, in fact, substantially above the vapor pressure as determined previously from rate of vaporization and from ablation measurements, as illustrated by points plotted in Figure 13 labeled 'No boiling at stagnation point.' Under different test conditions, however, namely substantially lower pressure, the melt flow suddenly boils as it moves radially outward over the front face and encounters the expansion
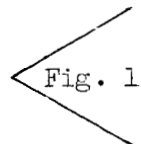
at the shoulder of the model. Here the melt suddenly enters a region of pressure much lower than the stagnation pressure, and flash boiling occurs if the shoulder pressure (pressure just behind the shoulder) is less than the boiling pressure. When it does, it follows that the vapor pressure at the shoulder temperature would be greater than the shoulder pressure. Such observations therefore provide a lower limit to the vapor pressure. An example of this nature is illustrated by the model in Figure 12(c) on which sudden and extensive frothing, interpreted as boiling, obviously occurred as soon as the melt flow reached the shoulder. The corresponding data point is illustrated in Figure 13 labeled 'Boiling at shoulder' with arrow pointing upward, indicating that the conditions for boiling lie at or above this point. It is seen that this observation also is consistent with the vapor pressure $P_v(\dot{m})$ and that these observations of boiling yield results which bracket concordantly the P_v data obtained from other methods of measurement.

BEARING OF VAPOR PRESSURE ON TEKTITE TRAJECTORIES
DETERMINED FROM AERODYNAMIC ANALYSIS

The effect of vaporization on ablation in hypervelocity flight is important indeed. Per unit mass ablated, vaporization absorbs much more heat than does melting: Heating tektite glass to a temperature at which it is fluid absorbs about 600 cal/g; whereas, vaporization absorbs directly about 3000 cal/g, plus indirectly an additional amount due to a 'blockage' effect. The blockage is

a pure aerodynamic effect in which the vaporized molecules diffuse into the boundary layer and alter there the temperature and velocity profiles in such a manner that the rate of convective heating at the surface is reduced. Such a heat blockage effect readily can dominate all others if a sufficient fraction of the material vaporizes; blockage, in fact, is a fundamental mechanism behind the efficient operation of heat shield materials on spacecraft and ballistic missiles. It follows that any increase in vapor pressure would increase the amount of vaporization relative to melting, and this would bring about a threefold effect: (1) more heat would be absorbed directly by the process of vaporization, (2) an additional amount of heat would be blocked from reaching the surface, and (3) the greater vaporization would reduce the surface temperature, thus increase the glass viscosity, and reduce the rate of melt-flow run off. Each of these three effects would contribute toward a lesser amount of ablation. Therefore, an increase in the vapor pressure for a given trajectory would result in a reduced amount of recession at the stagnation point.

One of the principal problems in the analysis of tektite ablation is that of determining what trajectories are compatible with the observed amount of stagnation-point recession y_s as measured on australites, that is, what combinations of initial velocity V_i and initial angle of entry γ_i into the atmosphere would produce the observed ablation (y_s typically about 1 cm). These two initial conditions determine the trajectory, and the

trajectory determines whether the tektites came from some point on the earth, or the moon, or a more distant place in the solar system. Both the velocity and angle of entry affect markedly the amount of ablation. That an increase in V_i would increase the ablation is rather obvious; but the fact that a decrease in γ_i (measured relative to the horizontal) also would markedly increase the amount of ablation may not be as obvious to one unfamiliar with atmosphere entry aerodynamics, and requires some explanation. The magnitude of the effect of γ_i on y_s can be illustrated by comparing the two extremes of shallow grazing entry and vertical descent. In a grazing entry the decelerations are much less than in vertical descent (about 10 g maximum compared to 350); the duration of ablation is much more (about 2 min compared to 5 sec), and the total amount of heat which must be absorbed is also much more (about 10 times that for vertical entry). In view of the much greater heat to be absorbed in shallow entries it follows that, for any given initial velocity, much more ablation would occur in a shallow grazing entry than in vertical descent.

From the foregoing it readily follows that if the amount of ablation on a tektite is known, then the trajectory determined from the use of a vapor pressure much higher than the true value will, for any given V_i, be much more shallow than the true trajectory. If the particular vapor pressure used in such calculations happens to be many orders of magnitude too high, such as is the bubble pressure $P_v(b)$ of Walter, then the tektite trajectories determined

therefrom would correspond to extremely shallow flight paths, very near the overshoot boundary. These circumstances explain why Adams and Huffaker [1964], who employed a vapor pressure based on Walter's preliminary measurements (nearly as high as his final bubble-pressure measurements), calculated that grazing trajectories near the overshoot limit would correspond to the amount of ablation observed on australites. Inasmuch as the hypothesis of tektite origin as ablation drops from a parent body is only possible with such grazing trajectories, they purported to represent their aerodynamic calculations as a confirmation of this hypothesis. Since their vapor pressure is greatly in error, their calculated results are erroneous, and therefore provide no support for the shallow entry hypothesis.

In regard to the absence of support from aerodynamic evidence for grazing tektite trajectories it should be noted that Adams and Huffaker [1962 and 1964] disregard the aerodynamic evidence provided by ring wave spacing, by the thickness of the melt layer, by the amount of deceleration determined from flange flattening, and by the depth of penetration of residual aerothermal stresses. Each of these four other independent sources of aerodynamic evidence contradicts the hypothesis of very shallow tektite trajectories and corresponds instead to relatively steep trajectories [Chapman and Larson, 1963; Chapman, 1964]. If Adams and Huffaker [1962] were to use the vapor pressure corresponding to the present measurements, which differ little from that for silica, then they would obtain

for entry at the earth's escape velocity of 11 km/sec (the initial
entry velocity objects would have coming from the moon) an entry angle
inclined about 30° to the horizontal, in approximate agreement with
the results of Chapman and Larson.

Inasmuch as the use of the vapor-pressure function $P_V(b)$,
which is from a hundred to a million times too high, results in a
change in entry angle from about 5° to 30°, it follows that an error
in vapor pressure of only a factor of about ±3 would result in
relatively small uncertainties in the trajectories determined from
aerodynamic analysis. Thus knowledge of P_V to within such a
factor is regarded as adequate for determining trajectories.

SUMMARY OF RESULTS AND CONCLUDING REMARKS

A summary is presented in Figure 13 of the experimental data
on tektite vapor pressure as determined from measurements of rate
of vaporization relative to different standards, from the rate of
ablation in an arc jet, from the mass loss in an arc jet, and from
the several observations of either boiling or no boiling. A least-
squares fit of a straight line through the various data points
corresponds to the equation

$$\ln P_V(\text{atm}) = \frac{-57,400}{T(°K)} + 18.50$$

This equation, representing the best available data for tektite
vapor pressure, is shown by the dashed line in Figure 13. It does
not differ greatly either from our original $P_V(\dot{m})$ data, or from

the vapor pressure of pure silica. Perhaps the latter observation should not be surprising, inasmuch as tektite glass is composed mainly of silica.

It is significant to observe that the above equation for vapor pressure is consistent with the Clapeyron-Clausius equation of thermodynamics $H_V = (RT^2/M)(d \ln P_V/dT)$ which relates the heat of vaporization H_V to the molecular weight M and to the slope of the vapor pressure curve. Differentiation of our equation above for P_V yields $H_V = 57,400 \ R/M$; with $M = 40$ g/mole, an approximate value for tektite glass (dissociated at the temperature range of interest), we obtain $H_V = 2850$ cal/g. This is reasonably close to the value of about 3000 cal/g expected for tektite glass: The value for pure silica is 3050 cal/g, while that of alumina is somewhat higher, and that of the other oxides comprising tektite glass is somewhat lower. In contrast, the much smaller slope of Walter's bubble pressure curve would yield from the Clapeyron-Clausius equation an H_V of only 600 cal/g, which obviously is far too low, and the equation of Adams and Huffaker [1964, their equation (1), p_{V3} in their notation] would yield, at temperatures above 2600°K, a negative value for H_V, which is impossible.

The principal application of vapor pressure data is involved in the determination of the atmosphere entry trajectories of tektites, and in the conclusion drawn therefrom of tektite flight along trajectories coming directly from the moon [Chapman and Larson, 1963]. In comparison to the equation which they employed

(namely, $\ln P_V = -57,800/T + 19.1$) the above equation for P_V yields
values lower by a factor of about 2 to 3, and would yield therefore
trajectories slightly steeper than those previously calculated.
The lower boundary of the trajectory domain recently determined by
Chapman [1964] was computed for $P_V = 0.5\ P_V(\dot{m})$; this boundary would
correspond very closely to trajectories proper to the new vapor
pressure equation. The shallow grazing trajectories recently cal-
culated by Adams [1964] however, were based upon a much higher
vapor pressure, under the presumption that Walter's bubble pressure
represented vapor pressure; these very shallow trajectories are
erroneous, inasmuch as it has been shown that large errors in the
amount of ablation, and in the mass vaporized during the ablation
process, are introduced if Walter's bubble pressure is used for
vapor pressure.

Walter's [1964] measurements of bubble pressure in tektite glass
must be interpreted as measurements primarily of the pressure of
some foreign gas or gases rather than the pressure of tektite vapor.
Foreign gases could come from any of several sources, such as
dissolved gases in the tektite glass, or gases adsorbed on the surface
during the preparation in the laboratory, or from some relatively
volatile impurity. Since many substances upon heating bubble before
they boil, the fact that tektite bubble-pressure measurements do not
represent tektite vapor pressure is not regarded as surprising.

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SKETCH AND FIGURE LEGENDS

Sketch (a). Log ambient pressure.

Fig. 1. Discrepancy in reported vapor-pressure measurements of tektite glass.

Fig. 2. High-temperature furnace.

Fig. 3. Comparison of vaporization mass loss for various liquids.

Fig. 4. Linear dependence of vapor pressure on rate of vaporization at constant aerothermal conditions.

Fig. 5. Mass-loss variation with pressure indicating diffusion-controlled vaporization.

Fig. 6. Rate of vaporization of gold, silver, silica, and tektite glass, $T = 1700^{\circ}K$, $P = 10^{-4}$ atm.

Fig. 7. P_V for tektite glass measured relative to different standards compared with P_V obtained using incipient bubbling method.

Fig. 8. Comparison of measured temperature with that computed for various vapor pressures.

Fig. 9. Comparison of measured mass loss with that computed for various vapor pressures.

Fig. 10. Comparison of measured amount of ablation with that computed for various vapor pressures.

Fig. 11. Comparison of measured and computed amount of ablation; $h_S = 11,000$ cal/g, $V = 9.6$ km/sec, $P_S = 0.52$ atm, $q_S = 760$ cal/cm^{2}sec.

Fig. 12. Observations of boiling in arc-jet experiments. (a)

Rizalite, locality Bugad Babuy, Luzon, sp. gr. 2.437;

$P_S = 0.08$ atm, $T_S = 2310^O$K, no boiling. (b) Australite,

locality Lake Wilson-Mt. Davies area, sp. gr. 2.452;

$P_S = 0.05$ atm, $T_S = 2310^O$K, no boiling. (c) Australite,

locality Lake Wilson-Mt. Davies area, sp. gr. 2.423;

$P_S = 0.022$ atm, $T_S = 2300^O$K, boiling at shoulder.

Fig. 13. Summary of P_V data for tektite glass as determined

from various experiments. Circle symbols are from vaporization

rates (Fig. 7).

Sketch (a)

TEMPERATURE, °K

P_v (b) - FROM MEASUREMENTS OF INCIPIENT BUBBLING (WALTER)

P_v ($\dot{m}$) - FROM MASS LOSS MEASUREMENTS RELATIVE TO SILICA (CENTOLANZI)

$$P_v(\dot{m}) = \exp\left[19.1 - \frac{57,800}{T}\right]$$

RECIPROCAL OF TEMPERATURE, $10^4/T(°K)$

Fig. 1

0 1 2 3 4
cm

WINDOW

BLACK BODY
HOLE

WINDOW

TANTALUM HEATING
ELEMENT

TEST SAMPLE

RADIATION SHIELD

WATER-COOLED
ELECTRODE

COOLING COILS

Fig. 2

Fig. 3

Fig. 4

TEKTITE GLASS
T=2100°K

RANGE OF
MOST TESTS

MASS LOSS RATE, $\dot{m}$, gm/cm² min

PRESSURE, mmHg

Fig. 5

Fig. 6

Fig. 7

CALCULATED

$.1 P_v(\dot{m})$ and $P_v(\dot{m})$

$10 P_v(\dot{m})$

$100 P_v(\dot{m})$

$1000 P_v(\dot{m})$

$P_v(b)$

MEASURED

○ SYNTHETIC TEKTITE
□ SYNTHETIC TEKTITE
◇ AUSTRALITE
△ AUSTRALITE

BRIGHTNESS TEMPERATURE, °K

2200
2000
1800
1600
1400
1200
1000
800

TIME, sec
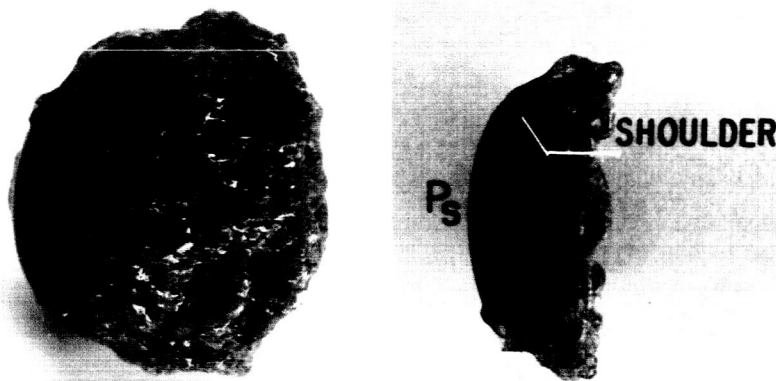
0   4   8   12   16   20

Fig. 8

Fig. 9

Fig. 10

Fig. 11

(a) RIZALITE; P_S = .08 atm
T_S = 2310° K; NO BOILING
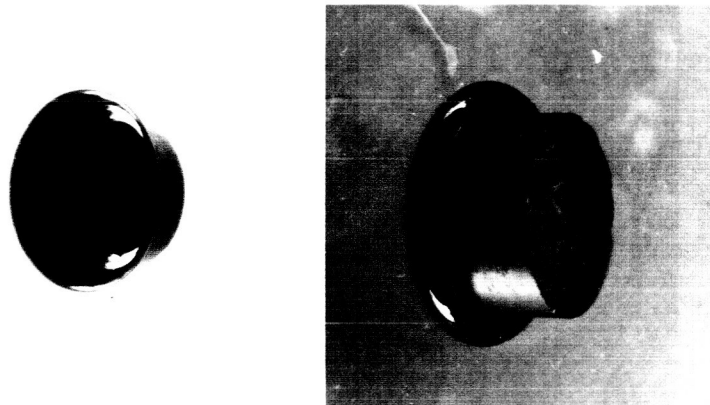
(b) AUSTRALITE; P_S = .05 atm
T_S = 2310° K; NO BOILING

(c) AUSTRALITE; P_S = .022 atm
T_S = 2300° K; BOILING AT SHOULDER

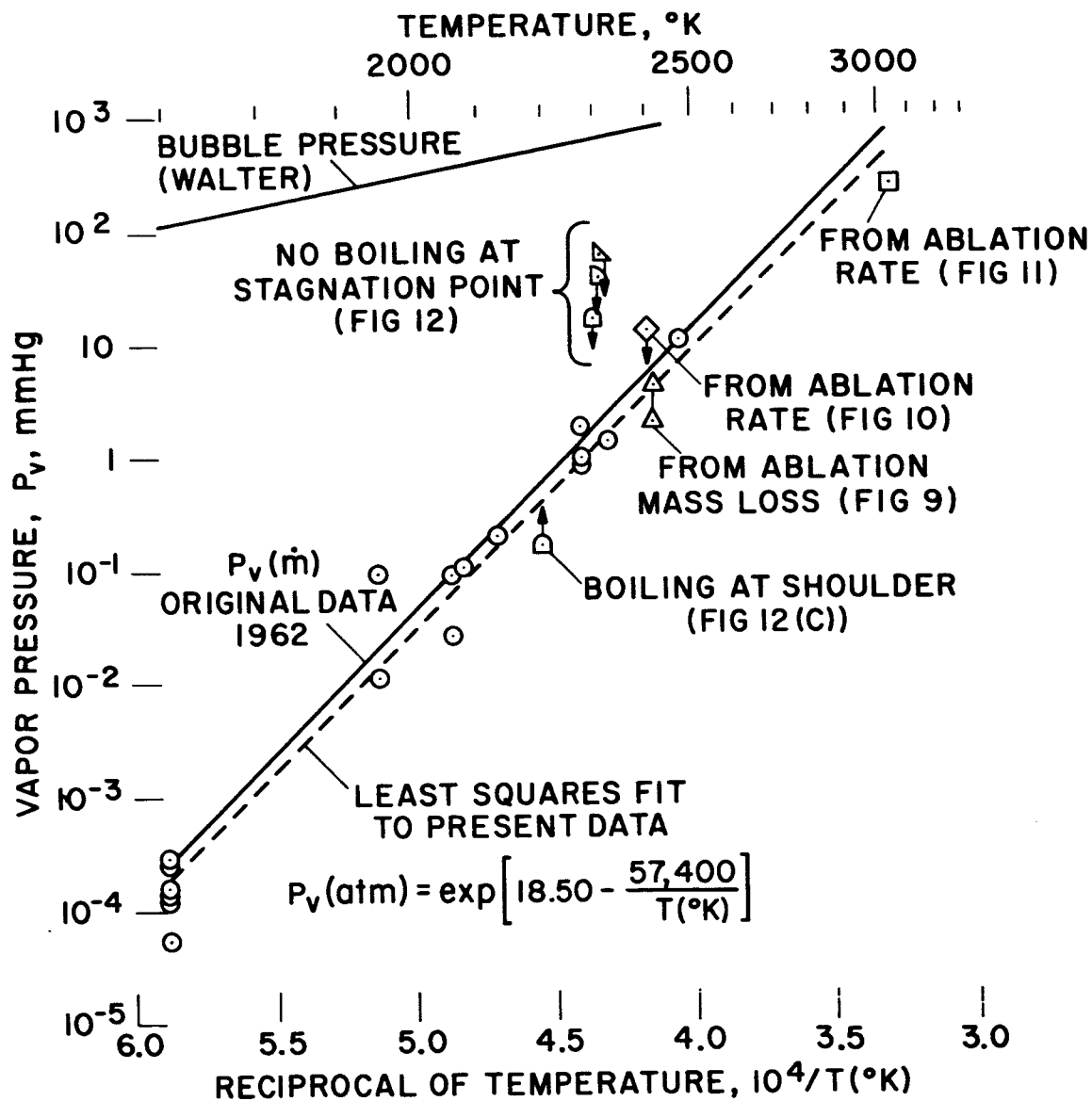Fig. 12

Fig. 13